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Assessment of Heavy Metal Content in Soils along Drini Bardhe River - Kosovo

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Abstract:

The assessment of heavy metals content in soil is required in order to evaluate soil quality and their environmental impact. Current study aims to evaluate heavy metals content and pollution in soils along Drini Bardhe river in Kosovo. Ten soil samples were collected along Drini Bardhe River to achieve the aims of this study. Heavy metals contents in soil samples were determined by using atomic absorption spectrophotometer (AAS). Evaluation of soil pollution was performed using the Enrichment Factor (EF) and Geo-accumulation Index (Igeo). Enrichment factor (Ef) calculations showed that soils have moderate enrichment for Cd and Ni, minimal enrichment for Cu, Cr, Mn and Pb, whereas no enrichment for Fe and Zn. Based on Geo-accumulation Index (Igeo) soils result strongly polluted with Cd, moderately to strongly polluted with Ni, moderately polluted with Cu, Cr, Pb and unpolluted to moderately polluted with Fe, Mn, and Zn. Background values given as 90th percentile were used also to evaluate the soils pollution with heavy metals. Occurrence of heavy metals in the studied soils indicates potential risk of some heavy metals as their amounts were over acceptable limits.

Keywords: Heavy metals, Ef, Igeo, pollution, soil, river.

1. Introduction

Human activities, including metal mining, smelting and finishing, coal combustion, refuse incineration, fossil fuel burning and agricultural practices have released countless tons of trace elements into the environment [12]. Thus soils and aquatic ecosystems continuously receive potentially hazardous trace elements from natural and anthropogenic sources, these pose serious threats because of their toxicity, persistence and tendency to bioaccumulation [10]. Elevated heavy metal concentrations in soil can have adverse impacts on crop production, food quality and safety, public health; therefore these concerns have attracted widespread attention [14, 11].

This study aims to estimate the level of heavy metals in the soils along Drini Bardhe river, to evaluate degree of soil pollution and to identify the possible impact of soil properties on heavy metal content and transfer into aquatic ecosystems. The assessment of heavy metals in soils would define anthropogenic and natural sources of them. The majority of heavy metal emissions from anthropogenic activities accumulate in river sediments, where they can be absorbed onto clays and other fine-grained materials [4], as well as in organic materials.

The measurement of elemental soil dust enrichment from heavy metals, can be carried out with different methods. The most important methods are the calculation of Geo-accumulation Index (Igeo) and Enrichment Factor (Ef). Both indices were used in this study to evaluate soil pollution level of eight heavy metals in ten sampling points in the soils along Drini Bardhe river.

2. Material and Methods

Study area

The investigated soils are along Drini Bardhe river in Kosovo (Figure 1). Ten representative sampling points were selected in this area to collect soil samples in order to estimate heavy metals concentrations. Soil samples were collected in 0-30 cm depth of soil profile.

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Figure 1. The study area and sampling points

Soil preparation and analysis

The collected soil samples were transported to the Laboratory of Agroenvironment and Ecology at Agricultural University of Tirana for their preparation and analysis. Samples were air dried and sieved with a 2 mm sieve and the fractions samples less than 2mm were used for further analysis.

Hydrometric method was used in determination of particle size distribution after removal of carbonates with HCl and disaggregation with dispersing agent sodium hexametaphosphate.

The pH of the soil is potentiometrically measured in the supernatant suspension of 1:5 soil:liquid mixture. This liquid is made up of a 1 M solution of KCl (pH/KCl) or water (pH/H_2O).

Total nitrogen, total phosphor and total potassium were determined spectrophotometrically after digestion of soils with H_2SO_4/Se/salicylic acid and H_2O_2. For total nitrogen, the absorbances of the samples were measured in 655nm, for TP in 880nm and flame emission photometry was used for K. Total content of heavy metals were extracted with 8 ml HNO3cc acid and 2 ml H_2O_2 33% and was micro waved for 25 minutes in 180^{o}C. The concentrations of heavy metals were determined by atomic absorption spectrophotometer (AAS). ISO standard methods were used in all analysis [5,6,7].

Assessment of heavy metal contamination

Evaluation of soil pollution degree with heavy metals was based on comparison with maximum acceptable levels set by the 86/278/EEC Directive [1], calculation of Enrichment Factor (EF) and Geo-accumulation Index (Igeo).

Enrichment Factor was calculated using the formula according to Li et al., [9]:

E_f = metal content in a given soil/metal content in earth crust *(1)*

Geo-accumulation Index was calculated using the equation from Huu et al., [4]:

I_{geo}= $\log_2$ (metal content in a given soil/metal content in the earth crust *1.5) *(2)*

1.5 is used to compensate for possible variations of the reference data due to lithogenic effects.

The heavy metals concentrations in the earth crust are taken from Rudnick and Gao [13], with respective values according to Taylor [14].

3. Results and Discussion

Soil properties

The obtained data of soil texture are shown in Table 1. The results showed that soils along Drini Bardhe river vary from silt loamy to clay loamy soils, but mainly were loamy soils, where the impact of clay, silt and sand in soil quality are equilibrated.

Table 1. The texture of soil samples

Soil sample	Sand (%)	Silt (%)	Clay (%)	Soil texture (according USDA)
TK-2	34.28	47.24	18.48	(Loam)
TK14	40.00	35.00	35.00	(Clay Loam)
TK14/1	44.54	30.81	24.65	(Loam)
TK11/2	42.87	42.85	14.28	(Loam)
TK11/12	51.13	36.65	12.22	(Loam)
TKH1	22.00	50.00	28.00	(Clay Loam)
TK2/1	16.27	69.44	14.30	(Silt Loam)
TK5	23.50	51.69	24.81	(Silt Loam)
TK8	41.07	48.77	10.16	(Loam)
TK11	44.95	40.78	14.27	(Loam)
TKB/50	20.11	65.55	14.34	(Clay Loam)

Others properties of studied soils are presented in Table 2. Based on the obtained data, soil pH was slightly acid to neutral, with interval of its mean values from 6.5 in 7.3. This parameter plays an important role in the mobility of heavy metals in soils and their bioavailability to crops [8]. Humus contents were at medium level and ranged from 1.3% in TK11/2 to 4.5% in TK5, respectively. Nitrogen concentration ranged from 0.1% to 0.2% in all soil samples, regardless the type of soils. Generally, cambisols have higher contents of organic carbon and nitrogen. Studied soil samples were, generally rich in available phosphor and potassium as their concentrations were high and ranged from 64.1 to 190.7 mg/kg and from 179.8 to 229.6 mg/kg, respectively.

Heavy metals contents in studied soils are shown in Table 3. Maximum values for heavy metals Cd (1.13 mg/kg), Mn (1200.64 mg/kg), Pb (38.16 mg/kg) and Zn (111.86 mg/kg) were obtained in soil sample TK14/1. Whereas, maximum values for Fe (30278.5 mg/kg) and Ni (253.76 mg/kg) were in soil sample TK H1. The maximum value for Cr (166.01 mg/kg) was in soil sample TK11 and for Cu (49.69 mg/kg) was in soil sample TKB50. Presence of these heavy metals in soil samples can be from natural sources, agricultural practices as chemicals use or from other anthropogenic inputs.

The background values determined in the soils were given as 90th percentile of the obtained values (Table 3). Indication of 90th percentile means that statistically 9 of 10 soil samples show low or the same element contents [3].

Enrichment factor and geo-accumulation index

Assessment of heavy metals pollution was defined using Enrichment Factor (EF) and Geo-accumulation Index (Igeo), based on the following categorization for Ef:

1) Ef ≤1 no enrichment; 2) 1 < Ef ≤3 minimal enrichment; 3) 3 < Ef ≤5 moderate enrichment; 4) 5 < Ef ≤10 moderately severe enrichment; 5) 10 < Ef ≤25 severe enrichment; 6) 25 < Ef ≤50 very severe enrichment; 7) Ef > 50 extremely severe enrichment);

and following categorization for Igeo:

1) Igeo < 0 unpolluted; 2) 0 ≤ Igeo < 1 unpolluted to moderately polluted; 3) 1 ≤ Igeo < 2 moderately polluted; 4) 2 ≤ Igeo < 3 moderately to strongly polluted; 5) 3 ≤ Igeo < 4 strongly polluted; 6) 4 ≤ Igeo < 5 strongly to very strongly polluted; 7) Igeo ≥ 5 very strongly polluted.

Table 2. The main properties of analyzed soil samples

Parameters	TK 2	TK 2/1	TK 5	TK 8	TK 11	TK 11/2	TK 14	TK 14/1	TK B50	TK H1	Min	Max	Mean	StDev
$pH_{(H2O)}$	7.4	7.4	7.1	7.2	7.3	7.3	7.2	7.2	7.4	7.2	7.1	7.4	7.3	0.1
$pH_{(KCl)}$	6.6	6.7	6.3	6.4	6.4	6.5	6.4	6.5	6.6	6.3	6.3	6.7	6.5	0.1
Humus (%)	3.9	2.1	4.3	3.1	1.9	1.3	2.9	3.2	2.0	2.5	1.3	4.3	2.7	0.9
N_{total} (%)	0.2	0.1	0.2	0.2	0.1	0.1	0.2	0.2	0.1	0.1	0.1	0.2	0.1	0.1
$P_2O_{5\ available}$ (mg/kg)	80.8	78.1	64.1	91.3	89.2	82.6	100.5	110.0	69.3	190.7	64.1	190.7	95.7	36.1
$K_2O_{available}$ (mg/kg)	213.0	209.4	217.1	186.0	186.9	198.9	229.6	226.3	179.8	219.0	179.8	229.6	206.6	17.7
P_{total} (mg/kg)	296.7	385.6	299.9	572.4	368.9	373.3	459.1	451.7	429.0	537.5	296.7	572.4	417.4	91.4
K_{total} (mg/kg)	3870.8	2821.7	4740.7	2828.2	2666.4	1927.1	5392.8	5294.1	2283.5	2548.5	1927.1	5392.8	3437.4	1286.9

Table 3. Heavy metals content, background values, Ef and Igeo of analyzed soil samples

Heavy metal	TK 2/1	TK 5	TK 8	TK 11	TK 11/2	TK 14	TK 14/1	TK B_{50}	TK H1	Mean	StDev	Background value	Average earth crust	(Ef)	Igeo
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		(as 90 %)	mg/kg		
Cd	0.58	0.54	0.74	0.52	0.53	0.99	1.13	0.56	0.66	0.69	0.22	1.018	0.098	7.04	3.40
Cu	35.41	24.07	29.23	35.54	35.1	25.35	41.62	49.69	48.73	36.08	9.25	48.922	25	1.44	1.11
Cr	151.67	130.31	28.88	166.01	150.23	73.75	62.41	163.92	153.57	120.08	51.18	164.338	85	1.41	1.08
Fe	25610.9	22195.4	21518.8	26117.6	25459.6	27315.1	28841.8	29783	30278.5	26346.74	3089.36	29882.1	35000	0.75	0.18
Mn	526.11	455.66	400.73	560.65	544.32	1051.85	1200.64	697.8	744.58	686.93	273.42	1081.608	540	1.27	0.93
Ni	238.91	253.2	33.46	230.77	247.21	75.92	60.11	247.05	253.76	182.265	95.19	253.312	44	4.14	2.64
Pb	19.83	22.7	22.11	17.38	20.88	31.93	38.16	19.56	23.8	24.04	6.70	33.176	17	1.41	1.08
Zn	55.56	47.15	56.28	50.53	57.12	88.75	111.86	55.57	63.36	65.13	21.23	93.372	71	0.92	0.46

According to the obtained Ef values (Table 3), the studied soils result: no enrichment for Fe and Zn, moderate enrichment for Ni, moderately severe enrichment for Cd and minimal enrichment for Cr, Mn and Pb.

Whereas, based on the Igeo (Table 3) result that these soils are strongly polluted with Cd, moderately to strongly polluted for Ni, moderately polluted for Cu, Cr and Pb and unpolluted to moderately polluted for Fe, Mn and Zn.

Furthermore, comparison of maximum values of obtained heavy metals concentration in analyzed soil samples and EU directive limit values (Table 4), indicated that the soils along Drini Bardhe river were polluted with Ni. Whereas, the concentrations of others heavy metals were under the limit value of this Directive.

Table 4. Comparison of maximum values of heavy metals concentrations in studied soils and EU Directive limit values [2]

Heavy metal	Maximum value in studied soils (mg/kg)	EU Directive 86/278 limit value (mg/kg)
Cd	1.13	3
Ni	253.76	75
Pb	38.16	300
Zn	111.86	300
Cu	46.69	140

Pollution of these soils by heavy metals especially with Ni, can be a potential source to contaminate water ecosystem of Drini Bardhe river. Thus, further studies are required for evaluation of this ecosystem and possible transfer of heavy metals to food chain.

4. Conclusions

Soils along Drini Bardhe river are mainly loamy and their properties are influenced by parent material. According to the Enrichment Factor these soils indicate no enrichment for Fe and Zn, moderate enrichment for Ni, moderately severe enrichment for Cd and minimal enrichment for Cr, Mn and Pb.

Data of Geo-accumulation Index showed that these soils are strongly polluted with Cd, moderately to strongly polluted for Ni, moderately polluted for Cu, Cr and Pb and unpolluted to moderately polluted for Fe, Mn and Zn.

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